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January 14, 1998

NASA Grants Officer
NASA Headquarters
300 E Street, SW
Washington, DC 20546

Dear Sir/Madam:

Enclosed please find the final report for NASA's grant NAGW-376, NAGW-3765, NAGW-4786, NAGW-5111, entitled "Physiological Ecology of Dimethylsulfoniopropionate (DMSP) and Dimethylsulfide (DMS) Production by Phytoplankton" (UM account 668920). This grant started at the University of Miami and, upon my move, was then transferred to Bigelow Laboratory for Ocean Sciences (NAGW-4786 and -5111). This final report is for both portions; a final report solely for the Miami portion was sent March 30, 1997.

Copies have been sent to the Grants Officer (Dr. Janet Campbell) and to the NASA Center for Aerospace Information.

Sincerely,

Patricia A. Matrai
Research Scientist

Enc.

Cc. J. Campbell, NASA Center for Aerospace Information, BLOS, RSMAS MAC, RSMAS Sponsored Team, University of Miami Sponsored Programs. ✓

“Physiological Ecology of Dimethylsulfoniopropionate (DMSP) and Dimethylsulfide (DMS) Production by Phytoplankton”

NAGW-376 and -3765 (University of Miami) and NAGW-4786 and -5111 (Bigelow Laboratory for Ocean Sciences), \$389,666, 11/93-6/97. This grant started at the University of Miami and was then transferred to Bigelow Laboratory for Ocean Sciences. This is a final report for the entire grant.

The main objectives of the previously funded work were: 1) to determine the rates of DMSP and DMS production as a function of phytoplankton growth rate, 2) to determine the light dependence (quantity and quality) of DMSP and DMS production by phytoplankton, and 3) to study intraspecific differences in DMSP and DMS production by phytoplankton.

Light-limited chemostats and batch cultures with the coccolithophore *Emiliania huxleyii* (clone 88E) were sampled, combining five growth rates, 2 light intensities and 3 photoperiods for their effects on intracellular and dissolved DMSP production. Cellular DMSP remained constant at growth rates lower than 0.8 d^{-1} and doubled at the highest growth rate. Dissolved DMSP also remained constant at growth rates lower than 0.8 d^{-1} , although at levels lower than DMSP_p by an order of magnitude. Cellular DMSP concentrations in the batch cultures did not change under increasing photoperiods and irradiance levels for cells growing exponentially or in stationary phase. In general, cellular DMSP was twice as high in the early stationary phase of growth as during exponential growth, regardless of light regime. No significant difference was observed in dissolved DMSP concentration in the medium regardless of growth phase and irradiance, although it was slightly higher at longer photoperiods. There was no DMS production by these light-limited, nutrient-replete cells.

Nitrate-limited chemostats with 3 species of phytoplankton, *E. huxleyii*, the dinoflagellate *Amphidinium carterae*, and the diatom *Thalassiosira pseudonana* grown axenically were followed at 3 or more growth rates. With increasing growth rate, DMSP levels decreased in the case of *T. pseudonana*, increased in the case of *A. carterae*, and remained essentially constant in the case of *E. huxleyii*. Cells at the higher growth rates were more nitrogen-replete intracellularly (i.e., higher cell quotas of DMSP). The current hypothesis is that DMSP would be present under nitrate-limited conditions while nitrogenous compounds would be present in nitrate-replete conditions. Interspecific variability is clearly present.

In addition, the variability in production rates due to intraspecific differences was examined by comparing axenic clones of *E. huxleyii*: clone 88E from the Gulf of Maine (bloom forming, coastal, temperate), and clone DWN 61/3/16 off Faroe Is. (bloom forming, open ocean, cold). These cells were grown in nitrate-limited chemostats, at four growth rates each. While subarctic clone 61/3/16 produced decreasing amounts of DMSP with increasing growth rate, temperate clone 88E behaved exactly the opposite. At each growth rate, photosynthetrons with blue and green-filtered light were used to determine the effect of light quantity and quality on DMSP and DMS production by nitrate-limited phytoplankton (DMS/P vs. irradiance experiments). The production of DMS and DMSP was a function of irradiance especially at growth rates higher than 0.6 d^{-1} . We modeled the production of DMS and DMSP by nitrate-limited cells exposed to a range of irradiance by using the chlorophyll-specific (or cell-specific) DMS(P) versus I curve parameters α , DMS(P)_{\max} , and β , estimated by fitting a hyperbolic function. DMS/P_{\max} [$\text{pmol DMS/P } \mu\text{g}^{-1} \text{chl } a \text{ h}^{-1}$] represents the

maximum chlorophyll-specific DMS or DMSP production rate, α [$\mu\text{mol DMS/P } \mu\text{g}^{-1} \text{ chl } a \text{ h}^{-1} (\mu\text{mol quanta m}^{-2} \text{ s}^{-1})^{-1}$] represents the slope of the curve at low light intensities, and β (same units as α) represents the degree of photoinhibition at high light intensities. It will be possible to combine these formulations of DMS and DMSP production as a function of biomass and irradiance with global estimates of these parameters measured by or derived from remote platforms, such as OCTS and SeaWiFS.

It is most likely that the production of DMSP is influenced by the interaction between light and nutrient levels as it occurs in nature. In the real ocean, it is most likely the combined effect of light and nutrients which determines the rate of production of DMSP and DMS by certain phytoplankton species. As the growth season progresses, conditions change from light-limited, nutrient replete (as in our light-limited chemostats) in late winter, to light- and nutrient-replete in early spring (as experienced by exponentially growing cells kept in batch cultures), to light-replete but nutrient-deplete (as in our nitrate-limited chemostats). In the case of *E. huxleyi* (clone 88E), which has been grown under all the above conditions, DMSP production remained constant under light-limited, nutrient-replete and increased at the highest growth rate (lower cell density, higher effective irradiance). Intracellular DMSP remained constant during exponential growth and increased slightly once cells were in stationary phase in batch culture conditions. At steady state, nitrate-limited, light-replete cells had increasing intracellular DMSP levels with increasing growth rate in the case of this clone (highest growth rate, lower cell density, higher nitrate cell quota).

To the extent that the role of these factors can be determined experimentally, the processes controlling the conversion of DMSP to DMS and DMS fluxes can be modeled and parameterized and the models, eventually, run on the basis of information obtained from remote sensing.

Finally, we examined the production of methyl bromide by phytoplankton cultures. Methyl bromide is another gas of climatic importance. Results from this part of our research are excerpted in this proposal and attached as a submitted manuscript in Appendix E. This work was the result of a Masters of Science research project by Stefania Saemundsdottir and was also part of the doctoral work of Daniel King, at the University of Miami (RSMAS). Another graduate student, Evan Howell, was involved in the analysis of the samples resulting from the first set of nitrate-limited chemostats during his first year. Two undergraduates, Andrew Tucker (University of Miami) and Jessica Nelson (University of New England) were involved in nitrate determinations and phytoplankton culturing, respectively. Jessica Nelson has been accepted into graduate school at SIO for next fall. Highlights of the results were included in the Introductory Oceanography courses for undergraduates that Matrai has taught at the Universities of Miami and New England, as a way of explaining the GAIA hypothesis and demonstrating the fact that phytoplankton are involved in the cycling of many elements, not just carbon and nitrogen.

Publications

- 1 **Matrai, P. A.**, M. Vernet, R. Hood, A. Jennings, D. Samundsdottir and E. Brody. 1995. "Light-dependent
2 production of DMS and carbon incorporation by polar strains of *Phaeocystis* spp." *Mar. Biol.*
3 124(1):157-167.
- 4 **Matrai, P. A.**, D. J. Cooper, D. Olson and E. S. Saltzman. 1996. "Oceanic DMS emissions associated with
5 frontal condition across a Gulf Stream meander." *J. of Marine Systems*, 7:1-8.

- Matrai, P. A.** and M. D. Keller. 1994. Total organic sulfur and dimethylsulfoniopropionate (DMSP) in marine phytoplankton: Intracellular variations. *Mar. Biol.*, 119:61-68.
- Saemundsdottir, S. and **P.A. Matrai**. 1998. Methyl bromide production by phytoplankton cultures, *Limnol. Oceanogr.*, in press.
- Matrai, P. A.**, J. Fritz, and E. Fernandez. 1998. Effect of day-length, irradiance and growth rate on the production of DMSP by the coccolithophore *Emiliana huxleyi*. *Mar. Ecol. Progr. Ser.*, subm.
- Matrai, P.A.** 1998. Phytoplankton production of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) as a function of irradiance and nitrate-limitation. In prep. for *Mar. Ecol. Progr. Ser.*

Presentations and Other Publications

- Newell, R. E., A. M. Thompson, D. D. Davis, P. Lagos and **P. A. Matrai**. 1993. "Pacific Exploratory Measurements-East (PEM-East), a natural complement to PEM-West for NASA/GTE." Workshop publication.
- Matrai, P.A.** 1994. Review of "Dimethyl Sulphide: Oceans, Atmosphere and Climate" G. Restelli and G. Angeletti [eds.], *Limnol. Oceanogr.*, 39:1497.
- Matrai, P.A.** 1995. "Light-dependent production of DMS and carbon incorporation by polar strains of *Phaeocystis* spp." Presented paper, First International DMSP Symposium, Mobile, AL, June.
- Matrai, P.A.** 1995. "Phytoplankton production of methyl bromide: Agriculture to ocean connection". Invited seminar, Bigelow Laboratory for Ocean Sciences, August.
- Matrai, P.A.** 1995. "Physiological Ecology of DMSP and DMS production by phytoplankton". Presented paper, NASA Aerosol Interdisciplinary Program Workshop, Columbia, MD, October.
- Kettle, J. and 15 co-authors, including **Matrai**. 1996. "Database of seasurface dimethylsulfide concentrations." Presented paper, AGU, San Francisco, CA, December.
- Matrai, P.A.**, J. Dacey, D. Erickson, E. Saltzman, T. Bates, J. Penner, and G. Wolfe. 1996. DMS climatology: seasonal-to-interannual, regional-to-global natural variability. A NASA-sponsored workshop on Ocean Biology, DMS, and the Earth's radiative budget. Held at Bigelow Laboratory for Ocean Sciences, August.
- Matrai, P.A.** 1997. "Phytoplankton production of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) as a function of irradiance and nitrate-limitation". Presented at ASLO Aquatic Sciences Meeting, Santa Fe, NM, February.
- Matrai, P.A.**, M.D. Keller and R. Kiene. 1997. "Production of glycine betaine (GBT) and dimethylsulfoniopropionate (DMSP) in nitrogen-limited chemostats cultures of marine phytoplankton". Presented paper, ASLO Aquatic Sciences, Santa Fe, NM, February.

Bullets

The work of Matrai (NAGW-376, NAGW-3765, NAGW-4786, NAGW-5111) had one main objective: Is the growth rate of phytoplankton as a function of the combined effect of nutrient (experimentally in constant supply) and light (quantity and quality) availability the determining factor in the production of DMSP and DMS in ocean waters? In addition, phytoplankton intraspecific differences in DMSP and DMS production as resulting from adaptation to different environmental conditions were examined. The results allowed us to decrease the number of leaps of faith that (still) have to be taken in the multistep chain of processes occurring between the biological source of DMS, the formation of sulfur aerosols, the resulting cloud albedo, and any

climate control if the proposed feedback between these compartments exists. To the extent that the role of these factors can be determined experimentally, the processes controlling the conversion of DMSP to DMS and DMS fluxes can be modeled and parameterized and the models, eventually, run on the basis of information obtained from remote sensing.

Service to NASA

I actively participated in the writing of the Natural Sources section of the report resulting from NASA's Aerosol Interdisciplinary Program Workshop held in Columbia, MD in October 95. I was the only senior oceanographer present at this workshop and specifically emphasized the connection between aerosols, oceans, and ocean color. It is hoped this document will serve to promote another funding period for such program.

I organized a workshop to prepare a white paper on future DMS research to be supported by Ocean Biogeochemistry, MTPE upon request of the Program Manager. NASA-funded scientists as well as scientist from the community at large were invited. Discussions resulted in a white paper presented to NASA MTPE.

As every year, I have reviewed proposals for the regular programs as well as the Graduate Fellowship program.